PHYSICAL REVIEW E VOLUME 52, NUMBER 4 OCTOBER 1995

Pressure of the hard-sphere solid

C. F. Tejero, M. S. Ripoll, and A. Pérez
Facultad de Ciencias Físicas, Universidad Complutense de Madrid, E-28040 Madrid, Spain
(Received 31 May 1995)

The pressure of the face-centered cubic hard-sphere crystal is analyzed using two different density functional theories: the generalized effective liquid approximation and the modified weighted density approximation. It is shown that in both theories the dominant contribution originates from the ideal part of the variational free energy. It is argued that in the region near close packing, reliable results can only be obtained by using the real-space version of these theories.

PACS number(s): 64.10.+h, 64.30.+t, 05.70.Ce

I. INTRODUCTION

The modern theory of freezing has been formulated in the last decade within the general density functional theory of nonuniform fluids [1,2]. One of its most celebrated applications concerns the determination of the thermodynamic properties and stability of the hard-sphere solid near the fluid-solid first-order transition. The results obtained from different density functional approaches for the freezing of hard spheres into a perfect fcc crystal are in good agreement with computer simulations (see [3] and references therein). Recently, Denton *et al.* [4] have extended previous studies based on the modified weighted density approximation (MWDA) [5] to the determination of the equation of state of the hard-sphere solid at high densities. They have examined, moreover, the relative magnitude of the contributions to the hard-sphere solid pressure from the ideal and excess parts of the variational free energy, showing that the former is positive in the whole density range while the latter is negative over a considerable range of densities. The aim of the present report is to analyze the findings of [4] within the generalized effective liquid approximation (GELA) [3], which also gives a good estimate of the thermodynamic properties and stability of the hard-sphere solid near the fluid-solid transition. Whereas the overall picture is found to be qualitatively the same, we have been unable to reproduce some of the quantitative results of [4]. A possible explanation for this will be given below.

In Sec. II we briefly review the GELA and the MWDA as applied to the hard-sphere solid. The general properties of the equation of state of the hard-sphere solid are analyzed in Sec. III. Our numerical results are presented in Sec. IV and discussed further in Sec. V. Our conclusions are gathered in Sec. VI.

II. GELA AND MWDA

The density functional theory of freezing [1,2] is based on the idea that the Helmholtz free energy of the solid, $F[\rho]$, is a unique functional of the local density of the solid $\rho(\mathbf{r})$, which can be split as

$$F[\rho] = F_{\rm id}[\rho] + F_{\rm ex}[\rho], \tag{2.1}$$

where

$$\beta F_{\rm id}[\rho] = \int d\mathbf{r}\, \rho(\mathbf{r}) \left\{\ln[\Lambda^3 \rho(\mathbf{r})] - 1\right\} \tag{2.2}$$

is the ideal contribution, with $\beta = 1/k_B T$ the inverse temperature and Λ the thermal de Broglie wavelength, and

$$\beta F_{\rm ex}[\rho] = -\int d\mathbf{r}\, \rho(\mathbf{r}) \int d\mathbf{r}'\, \rho(\mathbf{r}') \times \int_0^1 d\lambda\, (1-\lambda)\, c(\mathbf{r}, \mathbf{r}'; [\lambda\rho]) \tag{2.3}$$

is the excess term. In (2.3) $c(\mathbf{r}, \mathbf{r}'; [\lambda\rho])$ is the direct correlation function of the solid and λ $(0 \le \lambda \le 1)$ is a parameter defining a linear path of integration in the space of density functions $\rho_\lambda(\mathbf{r}) = \lambda\rho(\mathbf{r})$ connecting the zero reference density to the local density of the solid. The local equilibrium density of the solid is determined by minimizing $F[\rho]$ at constant average density. This variational procedure involves the direct correlation function of the solid which is the only unknown in (2.2) and (2.3) and hence some explicit approximation for the excess contribution $F_{\rm ex}[\rho]$ is required.

We are concerned here with a class of approximations (GELA [3] and MWDA [5]) which, based on the similarity of the thermodynamic properties of the solid and fluid phases, map the excess free energy per particle of the solid $f_{\rm ex}[\rho] \equiv F_{\rm ex}[\rho]/N$, where $N = \int d\mathbf{r}\rho(\mathbf{r})$ is the number of particles, onto that of an effective uniform fluid,

$$\beta f_{\rm ex}[\rho] = \psi(\hat\rho) = -\hat\rho \int d\mathbf{r} \int_0^1 d\lambda\, (1-\lambda)\, c(|\mathbf{r}|; \lambda\hat\rho), \tag{2.4}$$

where $\psi(\hat\rho) \equiv \beta f_{\rm ex}(\hat\rho)$, with $f_{\rm ex}(\hat\rho)$ and $c(|\mathbf{r}|; \lambda\hat\rho)$ denoting the excess free energy per particle and the direct correlation function of the corresponding uniform fluid, respectively, and $\hat\rho \equiv \hat\rho[\rho]$ being the effective liquid density which is used to represent the solid of density $\rho(\mathbf{r})$. Equation (2.4) is known as the thermodynamic mapping [3]. Note that, as we will be concerned below with the hard-sphere system, we have anticipated that $\psi(\hat{\rho})$, as indicated, is independent of the temperature.

The prescription for the effective liquid density $\hat{\rho}$ in the GELA is to identify the thermodynamic mapping (2.4) with the structural mapping (see [3] for details) defined by

$$\int d\mathbf{r}\,\rho(\mathbf{r}) \int d\mathbf{r}'\,\rho(\mathbf{r}')\,c(\mathbf{r},\mathbf{r}';[\rho]) = \int d\mathbf{r}\,\rho(\mathbf{r}) \int d\mathbf{r}'\,\rho(\mathbf{r}')\,c(|\mathbf{r}-\mathbf{r}'|;\hat{\rho}), \quad (2.5)$$

while in the MWDA the effective liquid density $\hat{\rho}$ has the form of a doubly weighted solid density (see [5] for details), i.e.,

$$\hat{\rho} = \frac{1}{N}\int d\mathbf{r}\,\rho(\mathbf{r}) \int d\mathbf{r}'\,\rho(\mathbf{r}')\,w(|\mathbf{r}-\mathbf{r}'|;\hat{\rho}), \quad (2.6)$$

with the weight function w in (2.6) given by

$$w(|\mathbf{r}|;\rho) = -\frac{1}{\rho\psi'(\rho)}\left[c(|\mathbf{r}|;\rho) + \frac{1}{V}\rho\psi''(\rho)\right], \quad (2.7)$$

where V is the volume of the system and, as usual, the prime denotes differentiation with respect to the argument.

In both approaches, a self-consistent equation for the determination of $\hat{\rho}$ in terms of the local density of the solid $\rho(\mathbf{r})$ and the direct correlation function of the liquid $c(|\mathbf{r}|;\rho)$ is obtained. The complicated functional dependence of $\hat{\rho}$ can be simplified if $\rho(\mathbf{r})$ is parametrized as a sum of normalized Gaussians centered about the lattice sites:

$$\rho(\mathbf{r}) = \left(\frac{\alpha}{\pi}\right)^{3/2} \sum_j e^{-\alpha(\mathbf{r}-\mathbf{r}_j)^2}, \quad (2.8)$$

where α is the inverse width of the Gaussians and the sum runs over the Bravais lattice vectors $\{\mathbf{r}_j\}$. Using this parametrization, the effective liquid density in the GELA is given by $\hat{\rho} = \hat{\rho}(\lambda = 1)$, where $\hat{\rho}(\lambda)$ is the unique solution of the differential equation [3]

$$\frac{\partial^2}{\partial\lambda^2}\left[\lambda\psi(\hat{\rho}(\lambda))\right] = \Phi(\hat{\rho}(\lambda);\rho,\alpha), \quad (2.9)$$

satisfying the initial conditions

$$[\hat{\rho}(\lambda)]_{\lambda=0} = 0, \qquad [\hat{\rho}'(\lambda)]_{\lambda=0} = \frac{1}{8}\Phi(0;\rho,\alpha), \quad (2.10)$$

where [6]

$$\Phi(\hat{\rho};\rho,\alpha) = -\sum_j \left(\frac{\alpha}{2\pi r_j^2}\right)^{1/2} \int_0^\infty dR\,R\,c(R;\hat{\rho}) \times \left[e^{-\alpha(R-r_j)^2/2} - e^{-\alpha(R+r_j)^2/2}\right], \quad (2.11)$$

with $r_j = |\mathbf{r}_j|$.

In the MWDA $\hat{\rho}$ is given instead by one of the solutions of the equation

$$2\hat{\rho}\psi'(\hat{\rho}) + \rho\hat{\rho}\psi''(\hat{\rho}) = \Phi(\hat{\rho};\rho,\alpha), \quad (2.12)$$

with $\rho = N/V$ denoting the average density of the solid.

The implementation of (2.9)–(2.12) for the hard-sphere solid can be easily undertaken since both the structure and the thermodynamics of the hard-sphere fluid are known from different theories. For the structure of the fluid phase (the direct correlation function) we have considered the analytic solution of the Percus-Yevick equation for hard spheres, from which the thermodynamics of the fluid phase (the excess free energy) has been found from (2.4). It can be shown that (2.12) is a quartic equation in $\hat{\rho}$ with either no real solution or two real solutions [7]. In the latter case we have found that only the smallest real solution leads to the existence of equilibrium solids, i.e., to a minimum in the solid free energy. Below we will refer to this solution of (2.12) as the real-space version of the MWDA whereas the method used in [4] will be referred to as the reciprocal-space or Fourier version of the MWDA. Solving (2.9) or (2.12), the effective liquid density $\hat{\rho} = \hat{\rho}(\rho,\alpha)$ depends parametrically on the average density of the solid ρ and on the inverse width of the Gaussians α. From the thermodynamic mapping (2.4) the excess free energy of the solid is finally determined as $\beta f_{\mathrm{ex}}[\rho] = \psi(\hat{\rho}(\rho,\alpha))$.

III. GENERAL PROPERTIES OF THE EQUATION OF STATE

For the large-α values where the equilibrium solids are found, the ideal free energy per particle of the solid phase (2.2) can be approximated, using (2.8), by its asymptotic large-α form

$$\beta f_{\mathrm{id}}[\rho] = \frac{3}{2}\left[\ln\left(\frac{\alpha}{\pi}\right) - 1\right] + 3\ln\Lambda - 1. \quad (3.1)$$

As stated above, the equilibrium solids are found by minimizing at constant average density the variational solid free energy

$$\beta\tilde{f}_S(\rho,\alpha) = \frac{3}{2}\left[\ln\left(\frac{\alpha}{\pi}\right) - 1\right] + 3\ln\Lambda - 1 + \psi(\hat{\rho}(\rho,\alpha)), \quad (3.2)$$

with respect to the inverse width of the Gaussians α for a given crystal structure, yielding

$$\frac{3}{2\alpha_m} + \frac{\partial\hat{\rho}(\rho,\alpha_m)}{\partial\alpha_m}\psi'(\hat{\rho}) = 0, \quad (3.3)$$

where α_m is the value of the inverse width parameter at the minimum.

Since $\psi'(\hat{\rho}) = [Z_L(\hat{\rho}) - 1]/\hat{\rho} > 0$, where Z_L denotes the compressibility factor of the hard-sphere fluid, (3.3) implies

$$\frac{\partial\hat{\rho}(\rho,\alpha_m)}{\partial\alpha_m} < 0, \quad (3.4)$$

i.e., the effective liquid density $\hat{\rho}$ decreases on increasing the localization of the hard spheres in the solid. This behavior is the one found for sufficiently high densities in the MWDA [5] and in the GELA [3]. Note that for small-α values the asymptotic form used for the ideal part of the solid free energy (3.1) is not an accurate approximation for (2.2), so (3.4) cannot be inferred. We remark, moreover, that (3.4) is independent of the density functional approach used to map the solid into an effective liquid, whenever the effective liquid density $\hat{\rho}$ is determined from the thermodynamic mapping (2.4).

Equation (3.3) can be solved yielding $\alpha_m = \alpha_m(\rho)$, from which the free energy of the solid is finally determined as $\beta f_S(\rho) = \beta \tilde{f}_S(\rho, \alpha_m(\rho))$, i.e.,

$$\beta f_S(\rho) = \frac{3}{2}\left[\ln\left(\frac{\alpha_m(\rho)}{\pi}\right) - 1\right] + 3\ln\Lambda \\ -1 + \psi(\hat{\rho}(\rho, \alpha_m(\rho))). \tag{3.5}$$

In what follows, the effective liquid density $\hat{\rho}$ will be considered as either a function of two variables $\hat{\rho}(\rho, \alpha_m(\rho))$ or as a unique function of the density $\hat{\rho}(\rho)$.

The pressure P_S (or the compressibility factor Z_S) of the hard-sphere solid can be derived from (3.5), yielding

$$Z_S(\rho) = \frac{\beta P_S(\rho)}{\rho} = \rho\beta f_S'(\rho) \equiv Z_S^{(1)}(\rho) + Z_S^{(2)}(\rho), \tag{3.6}$$

where

$$Z_S^{(1)}(\rho) = \frac{3\rho}{2\alpha_m(\rho)}\alpha_m'(\rho) \tag{3.7}$$

is the contribution coming from the ideal-gas variational free energy and

$$Z_S^{(2)}(\rho) = \rho\psi'(\hat{\rho})\hat{\rho}'(\rho) \tag{3.8}$$

is the one coming from the excess variational free energy.

As a matter of fact, $Z_S^{(1)}$ is positive definite, because the localization of the hard spheres increases when increasing the average density of the solid, i.e.,

$$\alpha_m'(\rho) > 0. \tag{3.9}$$

The sign of $Z_S^{(2)}$ can be analyzed by splitting the total derivative $\hat{\rho}'(\rho)$ as

$$\hat{\rho}'(\rho) = \frac{\partial\hat{\rho}(\rho, \alpha_m)}{\partial\rho} + \frac{\partial\hat{\rho}(\rho, \alpha_m)}{\partial\alpha_m}\alpha_m'(\rho), \tag{3.10}$$

which when substituted in (3.8) leads to the following expression for the equation of state (3.6):

$$Z_S(\rho) = \rho\psi'(\hat{\rho})\frac{\partial\hat{\rho}(\rho, \alpha_m)}{\partial\rho}, \tag{3.11}$$

where the equilibrium condition (3.3) has been used. Since $Z_S(\rho) > 1$ and $\psi'(\hat{\rho}) > 0$, we have

$$\frac{\partial\hat{\rho}(\rho, \alpha_m)}{\partial\rho} > 0. \tag{3.12}$$

On the other hand, from (3.4) and (3.9) we find

$$\frac{\partial\hat{\rho}(\rho, \alpha_m)}{\partial\alpha_m}\alpha_m'(\rho) < 0, \tag{3.13}$$

independently of the map used to represent the solid. Therefore, $\hat{\rho}'(\rho)$, and hence $Z_S^{(2)}$, has no predetermined sign. In the numerical results presented in the next section we show that (3.10) has a zero for intermediate solid densities in the MWDA whereas it is always negative in the GELA.

IV. NUMERICAL RESULTS

We will consider the two theories (GELA and MWDA) separately. For convenience we will use the reduced variables $\alpha\sigma^2$ and $\eta = \pi\rho\sigma^3/6$, where η is the packing fraction of hard spheres of diameter σ.

A. GELA

We find that solutions of (3.3) start to appear for $\eta \geq 0.48$ and persist up to $\eta \lesssim \eta_{\rm cp}$, where $\eta_{\rm cp} = \pi\sqrt{2}/6 \simeq 0.74$ denotes the packing fraction at close packing of the fcc crystal. Since the low-density behavior was already discussed in [3,6], we will concentrate here on the high-

TABLE I. Inverse width of the Gaussians $\alpha_m\sigma^2$ and effective liquid density $\hat{\eta} = \pi\hat{\rho}\sigma^3/6$ of the hard-sphere fcc solid as obtained from the GELA (2.9) and the real-space MWDA (2.12) for various packing fractions. The direct correlation function and the free energy per particle of the fluid phase have been described by the Percus-Yevick approximation.

	GELA		MWDA	
η	$\alpha_m\sigma^2$	$\hat{\eta}$	$\alpha_m\sigma^2$	$\hat{\eta}$
0.50	56.4	0.331	72.5	0.291
0.51	68.0	0.323	82.2	0.288
0.52	80.9	0.317	93.2	0.286
0.53	95.6	0.313	105.6	0.283
0.54	112.7	0.309	119.8	0.281
0.55	132.8	0.305	136.3	0.280
0.56	156.6	0.302	155.5	0.278
0.57	185.1	0.300	178.0	0.277
0.58	219.9	0.297	204.9	0.276
0.59	262.4	0.295	237.4	0.275
0.60	315.3	0.293	277.1	0.275
0.61	381.8	0.291	326.0	0.274
0.62	467.3	0.290	387.8	0.274
0.63	578.6	0.288	466.9	0.273
0.64	727.8	0.286	569.3	0.274
0.65	932.1	0.285	710.5	0.273
0.66	1222	0.283	906.5	0.273
0.67	1652	0.282	1191	0.274
0.68	2322	0.281	1628	0.274
0.69	3448	0.280	2352	0.274
0.70	5542	0.279	3682	0.274
0.71	10094	0.278	6520	0.275

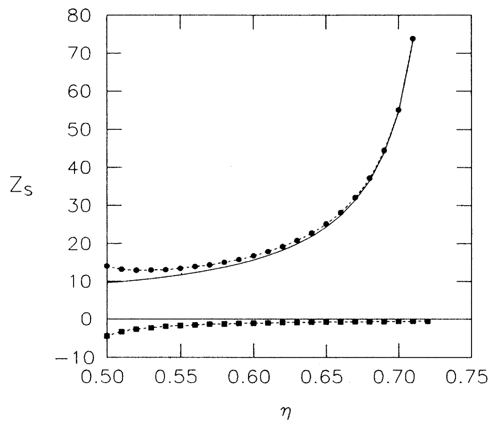

FIG. 1. Compressibility factor $Z_S(\rho)$ of the hard-sphere fcc solid (continuous line) vs the packing fraction η as obtained from the GELA. The contributions $Z_S^{(1)}$ and $Z_S^{(2)}$ [see (3.7) and (3.8)] are denoted by full dots and full squares, respectively. The direct correlation function and the free energy per particle of the fluid phase have been described by the Percus-Yevick approximation.

density solids only. We find that (3.9) is always satisfied (see Table I) whereas $\hat{\rho}'(\rho) \simeq 0$. Therefore the pressure is dominated (see Fig. 1) by $Z_S^{(1)}$. This is easily understood by observing that in the vicinity of $\eta_{\rm cp}$ the inverse width $\alpha_m\sigma^2$ shows a clear tendency to diverge (see Table I). The reason for this can be inferred from (2.11) since, for densities in the neighborhood of the close packing density, $\Phi(\hat{\rho};\rho,\alpha)$ is dominated by the $\exp[-\alpha(R-r_j)^2/2]$ terms with the smallest $(R-r_j)^2$ values, i.e., for $R\simeq 0$ and $R\simeq r_1$, with r_1 the nearest-neighbor distance. From Table I it can be found that $\alpha_m(r_1-\sigma)^2$ tends to a constant as η tends to $\eta_{\rm cp}$. This implies that near close packing, the mean-square deviation $\langle r^2\rangle = 3/2\alpha_m$ vanishes as $(r_1-\sigma)^2$, or that

$$\alpha_m\sigma^2 \simeq \left[\left(\frac{\eta_{\rm cp}}{\eta}\right)^{1/3} - 1\right]^{-2} \tag{4.1}$$

as $\eta \to \eta_{\rm cp}$. Using (4.1) for the determination of $Z_S^{(1)}$ and neglecting the small contribution of $Z_S^{(2)}$ yields

$$Z_S(\rho) = \left[1-\left(\frac{\eta}{\eta_{\rm cp}}\right)^{1/3}\right]^{-1} \quad (\eta\to\eta_{\rm cp}), \tag{4.2}$$

which is the well-known free-volume equation of state [8]. From Table II it is seen that our results are indeed close to satisfying (4.2)

B. MWDA

For small densities ($\eta < 0.63$) the behavior of the MWDA results of [4] is very similar to that of the above

TABLE II. Compressibility factor of the fcc hard-sphere solid as predicted by the GELA (2.9) and the real-space MWDA (2.12), and from free-volume theory [8] for various packing fractions η. The direct correlation function and the free energy per particle of the fluid phase have been described by the Percus-Yevick approximation. We also include the results obtained from the reciprocal-space MWDA of Denton *et al.* [4].

η	Z_S(GELA)	Z_S(MWDA)	Z_S(MWDA) [4]	Z_S(FVT)
0.50	9.7	7.9	7.9	8.2
0.51	10.0	8.2	8.2	8.6
0.52	10.3	8.6	8.6	9.0
0.53	10.7	9.0	9.0	9.5
0.54	11.2	9.4	9.4	10.0
0.55	11.7	10.0	10.0	10.6
0.56	12.3	10.6	10.6	11.2
0.57	13.0	11.2	11.2	12.0
0.58	13.8	12.0	12.0	12.8
0.59	14.7	12.9	12.9	13.7
0.60	15.7	13.9	13.9	14.8
0.61	16.9	15.1	15.1	16.0
0.62	18.3	16.5	16.5	17.4
0.63	19.9	18.1	18.1	19.1
0.64	21.9	20.1	20.2	21.1
0.65	24.4	22.5	22.9	23.5
0.66	27.4	25.5	26.6	26.6
0.67	31.3	29.4	31.6	30.5
0.68	36.5	34.6	38.8	35.7
0.69	43.7	41.8	50.3	43.0
0.70	54.8	52.9	70.8	53.9
0.71	71.6	69.7	114	71.9

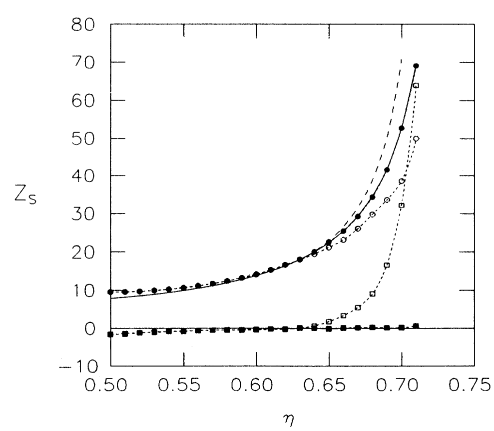

FIG. 2. The same as in Fig. 1 as obtained from the real-space MWDA. We also include in the figure the compressibility factor (dashed line) and the contributions $Z_S^{(1)}$ (open dots) and $Z_S^{(2)}$ (open squares) as obtained from the reciprocal-space MWDA [4].

GELA results. At higher densities a major difference occurs because $\hat{\rho}'(\rho)$, which in the GELA is always small and negative, starts to become positive in the MWDA (for $\eta \geq 0.63$) and to grow rapidly such that, at $\eta = 0.71$, $Z_S^{(1)}$ and $Z_S^{(2)}$ have about the same (positive) magnitude. In order to see whether this behavior is specific to the MWDA, we have tried to reproduce the results of [4] by starting from the real-space version (2.12). For $\eta \leq 0.63$ very good agreement with [4] was found (see Table II), but for $\eta > 0.63$ large differences appear. The qualitative behavior of $\hat{\rho}'(\rho)$ is still the same (e.g., it vanishes at $\eta \simeq 0.63$) but now we find its absolute value to be always small (see Fig. 2 and Table II). We tentatively ascribe these differences to the use in [4] of Fourier methods whose oscillatory convergence is very slow for densities near close packing, where α_m diverges [cf. (4.1)], whereas in the real-space method the behavior of (2.11) is dominated at these densities by the first nearest-neighbor shell.

V. PHYSICAL INTERPRETATION

From the real-space results of both the GELA (2.9) and the MWDA (2.12) we find that the equation of state of the hard-sphere crystal is dominated, at high densities, by $Z_S^{(1)}$. This term originates from the ideal-gas term of the variational free energy and therefore was termed "ideal-gas pressure" in [4]. This nomenclature is, however, somewhat misleading because once the variational principle (3.3) is used the "ideal-gas" and "excess" free energies become related to each other. Indeed, using (3.3) we can rewrite this "ideal-gas pressure" $Z_S^{(1)}$ in terms of the excess free energy, viz.,

$$Z_S^{(1)} = -\rho\alpha_m'(\rho)\frac{\partial\hat{\rho}(\rho,\alpha_m)}{\partial\alpha_m}\psi'(\hat{\rho}), \tag{5.1}$$

or else write the total pressure entirely in terms of the excess free energy only [see (3.11)].

In both the GELA and the real-space MWDA it is found that $Z_S^{(2)}$ is negative over a considerable range of densities ($0.46 < \eta < 0.63$ in the MWDA and $0.48 < \eta \lesssim \eta_{\rm cp}$ in the GELA) and always small. The negative sign of this "excess pressure" (as it was termed in [4]) was interpreted in [4] as implying the presence of an "effective" attraction. This notion of an effective attraction operating in the hard-sphere solid, but not in the hard-sphere fluid, remains, however, somewhat vague. If it is assumed to mean the potential of mean force as in [9], then this potential will always oscillate as a result of the formation of neighboring shells around the central particle as described by any typical correlation function for sufficiently high densities. If, on the contrary, one is referring to the depletion potential of [10] then one requires the presence of at least two different species of particles with the "depletion attraction" due to the expulsion of a shell of small particles around a central large particle. Moreover, in both these cases no distinction can be made between the high-density fluid phase and the solid phase, whereas the "effective attraction" of [4] is supposed to operate only in the solid phase.

VI. CONCLUSIONS

The equation of state of the fcc hard-sphere crystal was analyzed using two different density functional theories, the GELA and the MWDA. At densities near close packing the results of [4] could not be reproduced by using the real-space version of the MWDA embodied in (2.12). The results of (2.12) do, however, agree well with those of the GELA of (2.9). Both predict that the pressure of the hard-sphere crystal is dominated by the contribution coming from the ideal-gas variational free energy while the contribution from the excess variational free energy is always small in magnitude.

ACKNOWLEDGMENTS

We are grateful to M. Baus for useful discussions. C. F. Tejero acknowledges the DGICYT (Spain) (PB91-0378) for financial support.

[1] M. Baus, J. Phys. Condens. Matter **2**, 2111 (1990).
[2] R. Evans, in *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson (Dekker, New York, 1992), p. 85.
[3] J. F. Lutsko and M. Baus, Phys. Rev. Lett. **64**, 761 (1990); Phys. Rev. A **41**, 6647 (1990).
[4] A. R. Denton, N. W. Ashcroft, and W. A. Curtin, Phys. Rev. E **51**, 65 (1995).
[5] A. R. Denton and N. W. Ashcroft, Phys. Rev. A **39**, 4701 (1989).
[6] C. F. Tejero and J. A. Cuesta, Phys. Rev. E **47**, 490 (1993).
[7] A. Kyrlidis and R. A. Brown, Phys. Rev. A **44**, 8141 (1991).
[8] T. M. Reed and K. E. Gubbins, *Applied Statistical Mechanics* (McGraw-Hill, Tokyo, 1973), p. 282.
[9] S. Shinomoto, J. Stat. Phys. **32**, 105 (1983).
[10] P. D. Kaplan, J. L. Rouke, A. G. Yodh, and D. J. Pine, Phys. Rev. Lett. **72**, 582 (1994).